

1 β ,3,4 β ,6 β ,8-Pentamethyl-9-*exo*-methylenetricyclo[4.4.0.0^{3,8}]decane-2,5-dione
(a Twistane Derivative)

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Abstract. C₁₆H₂₂O₂, monoclinic, $P2_1/c$, $a = 13.7451$ (16), $b = 8.9543$ (7), $c = 12.5206$ (19) Å, $\beta = 115.218$ (10)°, $Z = 4$, $D_c = 1.17$ Mg m⁻³, $R = 0.039$ for 1974 observed reflections. The molecule possesses the twistane (tricyclo[4.4.0.0^{3,8}]decane) ring skeleton with all six-membered rings in distorted twist-boat conformations. The C(1)–C(6) and C(3)–C(8) bridge distances are 1.585 (3) and 1.584 (3) Å, respectively.

Introduction. Recrystallization from *n*-hexane afforded well formed colourless prismatic crystals suitable for X-ray analysis. A series of precession photographs provided an initial unit cell and the Laue symmetry $P2/m$. A crystal of dimensions $ca\ 0.5 \times 0.3 \times 0.3$ mm was mounted on an Enraf–Nonius CAD-4 diffractometer with [011] approximately parallel to the φ axis. A least-squares analysis of the setting angles of 25 reflections ($15 < \theta < 20^\circ$, graphite-monochromated Mo $K\alpha$ radiation) provided accurate unit-cell parameters. Intensities were collected with an ω – 2θ scan, $\Delta\omega = (0.75 + 0.35 \tan \theta)^\circ$, with a 25% extension on each side of the scan for background determination, an aperture 4 mm high and $(1.5 + \tan \theta)$ mm wide, a pre-scan acceptance limit of 30σ at $10.06^\circ \text{ min}^{-1}$, and a maximum recording time of 70 s. Of 2740 recorded intensities out to $\theta = 26^\circ$, 1974 (72%) had $I/\sigma(I) \geq 3$ with $\sigma^2(I) = S + B + (0.04S)^2$ ($S = \text{scan count}$, $B = \text{background count}$). The intensities of three check reflections measured every 60 min each showed a steady increase over the 33 h X-ray exposure to 105% of their initial value; this was corrected for during data processing where Lorentz and polarization corrections were applied.

The structure was solved by direct methods using *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1978) with 493 $|E|$ values derived by a K -curve method (Ladd, 1978). All 18 non-hydrogen atoms were located from an E map and were refined as isotropic C for three cycles of full-matrix least squares, after which the O atoms were identified by abnormally low U values. Atomic scattering factors were taken from Cromer & Mann (1968). Following anisotropic refinement for C and O, the H atoms were located from a difference map and were assigned isotropic thermal

parameters with scattering factors from Stewart, Davidson & Simpson (1965). Full-matrix least-squares refinement of all atomic parameters using weights $w = 1/\sigma^2(F)$ gave $R = 0.043$ ($R = \sum |\Delta F|/\sum |F_o|$) for the

Table 1. Final positional parameters (fractional, $\times 10^5$ for C and O atoms, $\times 10^3$ for H atoms) with estimated standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	33539 (14)	–18141 (21)	37481 (15)
C(2)	29976 (14)	–4080 (22)	41476 (15)
C(3)	20425 (14)	2992 (20)	31397 (15)
C(4)	10972 (15)	–6553 (22)	31545 (16)
C(5)	14235 (14)	–22923 (22)	32347 (14)
C(6)	22916 (15)	–25813 (19)	28176 (15)
C(7)	19072 (16)	–16913 (20)	16598 (15)
C(8)	21759 (14)	–375 (19)	19671 (16)
C(9)	33686 (16)	794 (22)	22872 (18)
C(10)	39798 (16)	–11793 (28)	30739 (21)
C(11)	40451 (22)	–28033 (35)	47740 (23)
C(31)	19481 (27)	19513 (27)	33347 (25)
C(41)	7386 (22)	–2394 (38)	41136 (23)
C(61)	24339 (24)	–42361 (24)	26389 (25)
C(81)	14588 (21)	9499 (28)	9388 (20)
C(91)	38363 (28)	11307 (40)	19288 (30)
O(2)	34018 (12)	749 (19)	51439 (13)
O(5)	10135 (13)	–32569 (18)	35851 (14)
H(111)	436 (2)	–359 (3)	449 (2)
H(112)	462 (3)	–218 (3)	537 (3)
H(113)	362 (2)	–329 (3)	515 (3)
H(311)	204 (2)	215 (3)	416 (3)
H(312)	254 (3)	251 (3)	322 (2)
H(313)	124 (3)	232 (3)	279 (3)
H(4)	48 (2)	–53 (2)	236 (2)
H(411)	39 (2)	78 (3)	395 (2)
H(412)	135 (2)	–17 (3)	489 (2)
H(413)	21 (2)	–95 (4)	411 (3)
H(611)	172 (2)	–466 (3)	196 (2)
H(612)	306 (2)	–437 (3)	238 (2)
H(613)	261 (2)	–480 (3)	341 (2)
H(71)	112 (2)	–186 (2)	118 (2)
H(72)	226 (2)	–208 (2)	117 (2)
H(811)	151 (2)	64 (3)	24 (2)
H(812)	69 (2)	88 (3)	81 (2)
H(813)	168 (2)	200 (3)	109 (2)
H(911)	463 (3)	106 (3)	218 (3)
H(912)	347 (3)	191 (4)	148 (3)
H(101)	467 (2)	–85 (3)	365 (2)
H(102)	410 (2)	–200 (3)	258 (2)

observed reflections, with the ΔF values for the intense low-angle reflections indicating an extinction problem. The final refinements included all atomic parameters and an isotropic extinction parameter g (Becker & Coppens, 1974, 1975) and gave $R = 0.039$ for the 1974 observed reflections. The function minimized was $\sum w(|F_o| - |F_c|)^2$, the final values of $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ and g being 0.054 and $9.0(1) \times 10^4$, respectively, with $\sigma_1(\text{GOF}) = 1.91$.* No parameter changed by more than 0.002σ in the last cycle of least squares. A final difference Fourier synthesis showed random fluctuations up to $\pm 0.15 \text{ e } \text{\AA}^{-3}$. Final atomic coordinates are presented in Table 1.

Discussion. Examination of the base-induced chemistry of the tricyclic alcohol 5-hydroxy-1,3,4,6,8,9-hexamethyltricyclo[4.4.0.0^{3,8}]deca-3,7-dien-2-one (I) has provided a simple entry to compounds having the relatively inaccessible tricyclo[4.4.0.0^{3,8}]decane [twistane (Whitlock, 1962)] ring skeleton (Scheffer & Yiu-Fai Wong, 1979; Greenhough, Scheffer, Trotter & Yiu-Fai Wong, 1979). The X-ray analysis of one of the products of the base-catalysed acyloin rearrangement of (I) has allowed an unambiguous assignment of the structure of 1 β ,3,4 β ,6 β ,8-pentamethyl-9-*exo*-methylenetricyclo[4.4.0.0^{3,8}]decane-2,5-dione (II), and provided only the second example of an X-ray crystal structure determination of a twistane derivative (Yordy & Reusch, 1975; Barnett & Yordy, 1975). The structure of the heterocyclic nitrogen complex 4-azatricyclo[4.4.0.0^{3,8}]decan-5-one ('aza-twistanone') has also been reported (Ramakumar, Venkatesan & Weber, 1977).

The molecular structure of (II) is shown in Fig. 1, viewed so that the approximate D_2 symmetry of the decane skeleton is apparent. The torsion angles of the five unique six-membered rings (Fig. 2) show deviations of up to 11° from those of the idealized twist-boat (Bucourt & Hainaut, 1965), but are similar to those in 8-(*p*-bromobenzenesulphonyloxy)-1,10-dimethyltricyclo[4.4.0.0^{3,8}]decan-2-one (III) (Barnett & Yordy, 1975) and to those calculated for twistane itself [empirical force-field calculations (Engler, Androse & Schleyer, 1973)]. The average difference in torsional angles between (II) and (III) is 1° , with a maximum of 6° , despite the changes in substitution and C(5),C(9) hybridization. Compared to the calculated twistane values (Engler, Androse & Schleyer, 1973) the torsional angles in the C(9)–C(10)–C(1)–C(2)–C(3)–C(4)–C(5) and C(4)–C(5)–C(6)–C(7)–C(8)–C(9)–C(10) linkages are an average of 4° smaller here, with

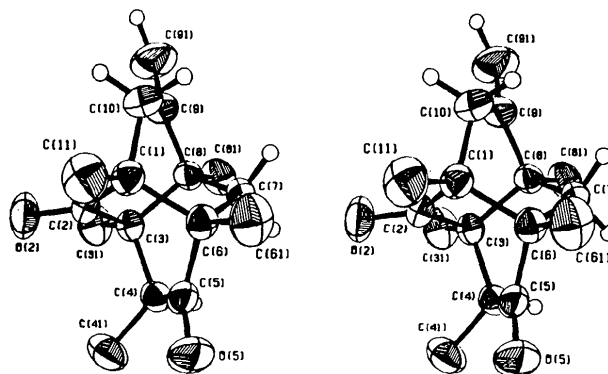


Fig. 1. Stereodiagram (Johnson, 1971) of the twistane derivative 1 β ,3,4 β ,6 β ,8-pentamethyl-9-*exo*-methylenetricyclo[4.4.0.0^{3,8}]decane-2,5-dione. Methyl hydrogens are omitted for clarity and thermal ellipsoids are at the 50% probability level. One of the *exo*-methylene H atoms is obscured by C(91).

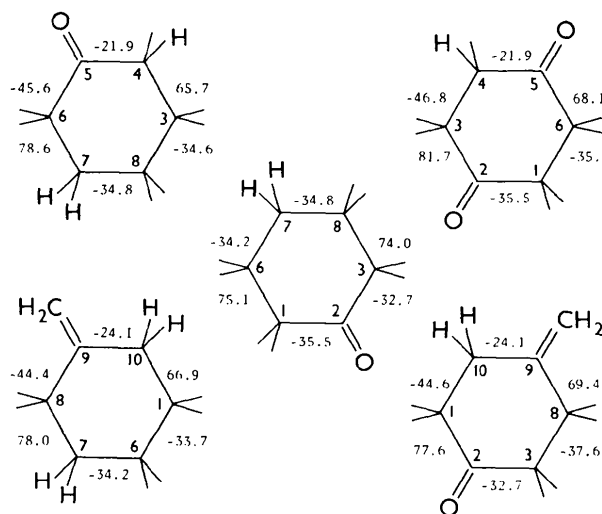


Fig. 2. Ring torsion angles ($^\circ$). Estimated standard deviations are 0.2° .

C(8)–C(9)–C(10)–C(1) greater by 4° . The D_2 symmetry of twistane is approximately retained in both (II) and (III); aza-twistanone is described as having approximate C_2 symmetry (Ramakumar, Venkatesan & Weber, 1977).

The bond distances and angles given in Tables 2 and 3 are indicative of the strain in this polycyclic system. The symmetrically bridged C(1), C(2), C(3), C(8), C(7), C(6) ring contains long C(1)–C(6) and C(3)–C(8) bridge distances of $1.585(3)$ and $1.584(3)$ \AA respectively, with angular deviations from the tetrahedral value at the bridgeheads up to 7.5° . The C(1)–C(6) and C(3)–C(8) distances in (III) (Barnett & Yordy, 1975) and aza-twistanone (Ramakumar, Venkatesan & Weber, 1977) are $1.563(7)$, $1.540(7)$ \AA and $1.572(4)$, $1.559(3)$ \AA , respectively. The endocyclic angles are generally less than expected values,

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34841 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances (Å) with *e.s.d.*'s in parentheses

C(1)–C(2)	1.511 (3)	C(2)–C(3)	1.519 (3)
C(3)–C(4)	1.563 (3)	C(1)–C(10)	1.548 (3)
C(4)–C(5)	1.524 (3)	C(9)–C(10)	1.497 (3)
C(5)–C(6)	1.515 (3)	C(8)–C(9)	1.517 (3)
C(6)–C(7)	1.537 (3)	C(7)–C(8)	1.535 (3)
C(1)–C(6)	1.585 (3)	C(3)–C(8)	1.584 (3)
C(2)–O(2)	1.209 (2)	C(5)–O(5)	1.211 (2)
C(3)–C(31)	1.514 (3)	C(1)–C(11)	1.516 (3)
C(6)–C(61)	1.524 (3)	C(8)–C(81)	1.527 (3)
C(4)–C(41)	1.526 (3)	C(9)–C(91)	1.322 (3)
C(11)–H(111)	0.97 (3)	C(61)–H(611)	1.06 (3)
C(11)–H(112)	1.00 (3)	C(61)–H(612)	1.05 (3)
C(11)–H(113)	0.99 (3)	C(61)–H(613)	1.02 (3)
C(31)–H(311)	1.00 (3)	C(81)–H(811)	0.95 (3)
C(31)–H(312)	1.02 (3)	C(81)–H(812)	1.00 (3)
C(31)–H(313)	0.98 (3)	C(81)–H(813)	0.98 (3)
C(41)–H(411)	1.01 (3)	C(91)–H(911)	1.00 (3)
C(41)–H(412)	0.98 (2)	C(91)–H(912)	0.90 (4)
C(41)–H(413)	0.97 (3)	C(10)–H(101)	0.97 (2)
C(7)–H(71)	1.00 (2)	C(10)–H(102)	1.02 (3)
C(7)–H(72)	1.00 (2)	C(4)–H(4)	1.00 (2)

Table 3. Inter-bond angles (°) with *e.s.d.*'s in parentheses

C(2)–C(1)–C(6)	106.1 (1)	C(5)–C(6)–C(1)	106.7 (1)
C(2)–C(1)–C(10)	102.0 (2)	C(5)–C(6)–C(7)	103.4 (1)
C(2)–C(1)–C(11)	112.4 (2)	C(5)–C(6)–C(61)	112.7 (2)
C(6)–C(1)–C(10)	108.1 (2)	C(1)–C(6)–C(7)	107.9 (1)
C(6)–C(1)–C(11)	114.7 (2)	C(1)–C(6)–C(61)	113.2 (2)
C(10)–C(1)–C(11)	112.5 (2)	C(7)–C(6)–C(61)	112.3 (2)
C(2)–C(3)–C(4)	101.0 (1)	C(9)–C(8)–C(7)	104.5 (2)
C(2)–C(3)–C(8)	106.9 (1)	C(9)–C(8)–C(3)	106.3 (1)
C(2)–C(3)–C(31)	112.1 (2)	C(9)–C(8)–C(81)	114.8 (2)
C(4)–C(3)–C(8)	109.4 (1)	C(7)–C(8)–C(3)	107.8 (1)
C(4)–C(3)–C(31)	113.8 (2)	C(7)–C(8)–C(81)	110.3 (2)
C(8)–C(3)–C(31)	112.8 (2)	C(3)–C(8)–C(81)	112.5 (2)
C(1)–C(2)–C(3)	111.1 (1)	C(4)–C(5)–C(6)	113.3 (1)
C(1)–C(2)–O(2)	124.6 (2)	C(4)–C(5)–O(5)	122.7 (2)
C(3)–C(2)–O(2)	124.3 (2)	C(6)–C(5)–O(5)	124.0 (2)
C(3)–C(4)–C(5)	107.7 (1)	C(8)–C(9)–C(10)	111.3 (2)
C(3)–C(4)–C(41)	115.2 (2)	C(8)–C(9)–C(91)	126.0 (2)
C(5)–C(4)–C(41)	111.6 (2)	C(10)–C(9)–C(91)	122.8 (2)
C(6)–C(7)–C(8)	108.3 (1)	C(1)–C(10)–C(9)	110.4 (2)

the sp^2 -hybridized C atoms C(2), C(5), and C(9) all having endocyclic angles approaching the tetrahedral value, as was found for the C(2) carbonyl group in (III) (Yordy & Reusch, 1975; Barnett & Yordy, 1975) and the C(5) carbonyl group in aza-twistanone (Ramakumar, Venkatesan & Weber, 1977). Twistane itself is not free from angle strain (Whitlock, 1962) and the geometries of the structurally characterized derivatives of twistane indicate the relief of torsional strain at

the expense of angle strain. The carbonyl group containing O(2) is slightly non-planar, C(2) deviating by 0.009 Å (4σ) from the mean plane of the group. The other carbonyl group and the alkene function are planar within experimental error. The methyl group at C(4) is pseudo-axial with respect to the C(3) to C(8) ring. The crystal structure consists of discrete molecules, with no C...C or C...O intermolecular distances less than 3.45 Å.

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